Solid-Fluid Equilibrium in Benzene-Hexafluorobenzene Mixtures: Congruent Melting from a Molecular Model

J. Schroer and P.A. Monson [C, S]
Department of Chemical Engineering, University of Massachusetts, Amherst, MA, U.S.A.

In order to design a feasible crystallization-based separation, it is important to know the solid-fluid equilibrium phase diagram. Phase diagrams offer visualization of the process and thermodynamic constraints due to the formation of eutectics and solid compounds. Because solid compound formation can be a barrier to traditional crystallization-based separations, identification of regions of the phase diagram where compound formation may occur is necessary. Unfortunately, classical thermodynamic theory is not capable of predicting the complex behavior of solid compound formation. The benzene-hexafluorobenzene system is interesting in that although the vapor-liquid equilibrium indicates a nearly ideal fluid mixture, the solid-fluid behavior exhibits a 1:1 solid compound that has a melting point over 18 degrees higher than either of the pure components. It is therefore an interesting test case for developing theories of solid-fluid equilibrium in aromatic systems. We have calculated the phase diagram of a quadrupolar hard sphere interaction site model for benzene-hexafluorobenzene mixtures. The model, which takes into account both fluid and solid phase phenomena, was studied using Monte Carlo simulation. The molecules in this mixture are similar in shape, yet have different pure component crystal structures and oppositely polarized quadrupole moments. The balance between the hard core repulsive forces and the electrostatic forces is the fundamental feature that underlies the phase diagrams of aromatic solids. Although many previous authors have speculated as to whether molecular packing or electrostatic interactions are the fundamental driving force for the stability of this compound, we show precisely the trade-offs between these interactions in our model and their role in determining the solid-fluid equilibrium phase diagram. The model correctly predicts the high stability and congruent melting of the 1:1 compound in the benzene-hexafluorobenzene system.